Integral relation between pair direct correlation function and density-density correlation function

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Direct correlation functions

Let's consider grand potential functional:

$$\Omega[\rho] = -kT\int \rho(\ln(\Lambda^3\rho)-1)d\mathbf{r} + \int u_{ext}\rho d\mathbf{r} - \mu\int \rho d\mathbf{r} + F_{\mathrm{int}\,ex} \quad (1.1)$$

Where $F_{\mathrm{int}\,ex}$ is excessive intrinsic free energy – energy due to the particle interactions

We may express $F_{\mathrm{int}\,ex}$ as $F_{\mathrm{int}\,ex} = -kT\int c^{(1)}(\mathbf{r})\rho d\mathbf{r}$ where $c^{(1)}(\mathbf{r})$ is single direct particle correlation function or as $F_{\mathrm{int}\,ex} = -kT\int c^{(2)}(\mathbf{r},\mathbf{r}')\rho(\mathbf{r})\rho(\mathbf{r}')d\mathbf{r}d\mathbf{r}'$ where $c^{(2)}(\mathbf{r},\mathbf{r}')$ is two-particle direct correlation function.

The definition for $c^{(1)}(\mathbf{r})$ and $c^{(2)}(\mathbf{r},\mathbf{r}')$ might be given as:

$$c^{(2)}(\mathbf{r},\mathbf{r}') = -\beta\frac{\delta^2 F_{\mathrm{int}.ex.}}{\delta\rho(\mathbf{r})\delta\rho(\mathbf{r}')}$$

$$c^{(1)}(\mathbf{r}) = -\beta\frac{\delta F_{\mathrm{int}.ex.}}{\delta\rho(\mathbf{r})}$$

In the equilibrium case we have $\frac{\delta\Omega[\rho]}{\delta\rho} = 0$. Taking derivative from (1.1):

$$\frac{\delta\Omega[\rho]}{\delta\rho(\mathbf{r})} = 0 = kT(\ln(\Lambda^3\rho)) + u_{ext} - \mu - kTc(\mathbf{r}) \qquad (1.2)$$

And we have $\rho = \frac{e^{\beta\mu}}{\Lambda^3}e^{-\beta u_{ext}(\mathbf{r})+c(\mathbf{r})}$

Pair density-density correlation function

One particle density function can be expressed as $\rho^{(1)}(\mathbf{r}) = \left\langle \sum_{i=1}^{N}\delta(\mathbf{r}-\mathbf{r_i})\right\rangle$ where triangular brackets mean averaging over configurational space:

$$\left\langle \sum_{i=1}^{N}\delta(\mathbf{r}-\mathbf{r_i})\right\rangle = \int \sum_{i=1}^{N}\delta(\mathbf{r}-\mathbf{r_i})P(\mathbf{r}_1,...,\mathbf{r}_N)d\mathbf{r}_1...d\mathbf{r}_N$$

We may define pair density correlation function as:

$$H(\mathbf{r},\mathbf{r}') = \left\langle \left(\sum_{i=1}^{N}\delta(\mathbf{r}-\mathbf{r}_i) - \rho^{(1)}(\mathbf{r})\right)\left(\sum_{j=1}^{N}\delta(\mathbf{r}'-\mathbf{r}_j) - \rho^{(1)}(\mathbf{r}')\right)\right\rangle$$

Opening the brackets we have:

$$H(\mathbf{r},\mathbf{r}') = \left\langle \sum_{i=1}^{N} \delta(\mathbf{r}-\mathbf{r}_i)\delta(\mathbf{r}'-\mathbf{r}_j) \right\rangle - \rho^{(1)}(\mathbf{r}) \left\langle \sum_{j=1}^{N} \delta(\mathbf{r}'-\mathbf{r}_j) \right\rangle - \left\langle \sum_{i=1}^{N} \delta(\mathbf{r}-\mathbf{r}_i) \right\rangle \rho^{(1)}(\mathbf{r}') + \rho^{(1)}(\mathbf{r})\rho^{(1)}(\mathbf{r}')$$

$$H(\mathbf{r},\mathbf{r}') = \left\langle \sum_{i=1}^{N} \sum_{j=1}^{N} \delta(\mathbf{r}-\mathbf{r}_i)\delta(\mathbf{r}'-\mathbf{r}_j) \right\rangle - \rho^{(1)}(\mathbf{r})\rho^{(1)}(\mathbf{r}')$$

we may write double sum as:

$$\left\langle \sum_{i=1}^{N} \sum_{j=1}^{N} \delta(\mathbf{r}-\mathbf{r}_i)\delta(\mathbf{r}'-\mathbf{r}_j) \right\rangle = \left\langle \sum_{i=1}^{N} \sum_{i\neq j}^{N} \delta(\mathbf{r}-\mathbf{r}_i)\delta(\mathbf{r}'-\mathbf{r}_j) \right\rangle + \left\langle \sum_{i=1}^{N} \delta(\mathbf{r}-\mathbf{r}_i)\delta(\mathbf{r}'-\mathbf{r}_i) \right\rangle \qquad (1.3)$$

The first term is pair probability density function

$$\left\langle \sum_{i=1}^{N} \sum_{i\neq j}^{N} \delta(\mathbf{r}-\mathbf{r}_i)\delta(\mathbf{r}'-\mathbf{r}_j) \right\rangle = \rho^{(2)}(\mathbf{r},\mathbf{r}')$$

In the second term we may use a relation: $\delta(\mathbf{r}-\mathbf{r}_i)\delta(\mathbf{r}'-\mathbf{r}_i) = \delta(\mathbf{r}-\mathbf{r}_i)\delta(\mathbf{r}-\mathbf{r}')$

We have

$$\left\langle \sum_{i=1}^{N} \delta(\mathbf{r}-\mathbf{r}_i)\delta(\mathbf{r}-\mathbf{r}') \right\rangle = \delta(\mathbf{r}-\mathbf{r}') \left\langle \sum_{i=1}^{N} \delta(\mathbf{r}-\mathbf{r}_i) \right\rangle = \delta(\mathbf{r}-\mathbf{r}')\rho^{(1)}(\mathbf{r})$$

And finally:

$$H(\mathbf{r},\mathbf{r}') = \rho^{(2)}(\mathbf{r},\mathbf{r}') + \delta(\mathbf{r}-\mathbf{r}')\rho(\mathbf{r}) - \rho^{(1)}(\mathbf{r})\rho^{(1)}(\mathbf{r}')$$

Using the definition of pair density correlation function

$$g(\mathbf{r},\mathbf{r}') = \frac{\rho^{(2)}(\mathbf{r},\mathbf{r}')}{\rho^{(1)}(\mathbf{r})\rho^{(1)}(\mathbf{r}')}$$

We have

$$H(\mathbf{r},\mathbf{r}') = \rho^{(1)}(\mathbf{r})\rho^{(1)}(\mathbf{r}')(g(\mathbf{r},\mathbf{r}')-1) + \delta(\mathbf{r}-\mathbf{r}')\rho(\mathbf{r}) = \rho^{(1)}(\mathbf{r})\rho^{(1)}(\mathbf{r}')h(\mathbf{r},\mathbf{r}') + \delta(\mathbf{r}-\mathbf{r}')\rho(\mathbf{r})$$

where $h(\mathbf{r},\mathbf{r}') = g(\mathbf{r},\mathbf{r}') - 1$

Relation between the direct and density-density correlations

In the presence of external field grand partition function is:

$$\Xi = \sum_{N=0}^{\infty} \frac{e^{\beta\mu N}}{\Lambda^{3N}} \frac{1}{N!} \int e^{-\beta\left(U_N + \sum u_{ext}(\mathbf{r_i})\right)} d\mathbf{r^N}$$

Grand potential can be expressed $\Omega = -kT \ln \Xi$

Let's take derivative from Ω:

$$\frac{\delta\Omega[\rho]}{\delta u_{ext}(\mathbf{r})} = -kT \frac{\delta \ln \Xi}{\delta\rho(\mathbf{r})} = -\frac{kT}{\Xi} \frac{\delta\Xi}{\delta\rho(\mathbf{r})} = \frac{-kT}{\Xi} \sum_{N=0}^{\infty} \frac{e^{\beta\mu N}}{\Lambda^{3N}} \frac{1}{N!} \int e^{-\beta\left(U_N + \sum u_{ext}(\mathbf{r_i})\right)} (-\beta) \sum \delta_{ext}(\mathbf{r}-\mathbf{r_i}) d\mathbf{r^N}$$

$$= \left\langle \sum \delta_{ext}(\mathbf{r}-\mathbf{r_i}) \right\rangle = \rho^{(1)}(\mathbf{r})$$

We also may see that $\frac{\delta\Xi}{\delta\rho(\mathbf{r})} = -\beta\Xi\rho^{(1)}(\mathbf{r})$

Taking second derivative:

$$\frac{\delta^2\Omega[\rho]}{\delta u_{ext}(\mathbf{r})\delta u_{ext}(\mathbf{r}')} = \frac{\delta\rho^{(1)}(\mathbf{r})}{\delta u_{ext}(\mathbf{r}')} =$$

$$\frac{-kT}{\Xi^2}\frac{\delta\Xi}{\delta\rho(\mathbf{r})}\frac{\delta\Xi}{\delta\rho(\mathbf{r}')} - \frac{kT}{\Xi}\sum_{N=0}^{\infty}\frac{e^{\beta\mu N}}{\Lambda^{3N}}\frac{1}{N!}\int e^{-\beta\left(U_N+\sum u_{ext}(\mathbf{r_i})\right)}(-\beta^2)\sum\delta(\mathbf{r}-\mathbf{r}_j)\sum\delta(\mathbf{r}-\mathbf{r_i})d\mathbf{r^N}$$

$$= \frac{-kT}{\Xi^2}\beta^2\Xi^2\rho(\mathbf{r})\rho(\mathbf{r}') + kT\beta^2\left\langle\sum\delta(\mathbf{r}-\mathbf{r}_j)\sum\delta(\mathbf{r}-\mathbf{r_i})\right\rangle$$

Using result (1.3) we have

$$\frac{\delta^2\Omega[\rho]}{\delta u_{ext}(\mathbf{r})\delta u_{ext}(\mathbf{r}')} = -\beta\left(\rho^{(2)}(\mathbf{r},\mathbf{r}') + \delta(\mathbf{r}-\mathbf{r}')\rho(\mathbf{r}) - \rho(\mathbf{r})\rho(\mathbf{r}')\right) = -\beta H(\mathbf{r},\mathbf{r}')$$

For the absence of external field we have uniform density and:

$$\left.\frac{\delta\rho^{(1)}(\mathbf{r})}{\delta u_{ext}(\mathbf{r}')}\right|_{u_{ext}(\mathbf{r}')=0} = -\beta\left(\rho^2 h(\mathbf{r},\mathbf{r}') + \rho\delta(\mathbf{r}-\mathbf{r}')\right) \qquad (1.4)$$

Taking the derivative from (1.2) we have

$$0 = \frac{kT}{\rho(\mathbf{r}')}\delta(\mathbf{r}-\mathbf{r}') + \frac{u_{ext}(\mathbf{r})}{\delta\rho(\mathbf{r}')} - kT\frac{\delta c(\mathbf{r})}{\delta\rho(\mathbf{r}')}$$

Using the definition of direct correlation function we may see $\frac{\delta c(\mathbf{r})}{\delta\rho(\mathbf{r}')} = c(\mathbf{r},\mathbf{r}')$

Thus we have

$$c(\mathbf{r},\mathbf{r}') = \beta\frac{u_{ext}(\mathbf{r})}{\delta\rho(\mathbf{r}')} + \frac{\delta(\mathbf{r}-\mathbf{r}')}{\rho(\mathbf{r}')}$$

and

$$\frac{u_{ext}(\mathbf{r})}{\delta\rho(\mathbf{r}')} = kTc(\mathbf{r},\mathbf{r}') - kT\frac{\delta(\mathbf{r}-\mathbf{r}')}{\rho(\mathbf{r}')} \qquad (1.5)$$

Now we may use chain rule for functional derivatives, namely:

$$\delta(r-r') = \frac{\delta u_{ext}(\mathbf{r})}{\delta u_{ext}(\mathbf{r}')} = \int\frac{\delta u_{ext}(\mathbf{r})}{\delta\rho(\mathbf{r}'')}\frac{\delta\rho(\mathbf{r}'')}{\delta u_{ext}(\mathbf{r}')}d\mathbf{r}''$$

Putting here expressions (1.5) and (1.4) we have

$$\delta(r-r') = -\beta\rho kT\int\left(c(\mathbf{r},\mathbf{r}'') - \frac{\delta(\mathbf{r}-\mathbf{r}'')}{\rho}\right)\left(\rho h(\mathbf{r},\mathbf{r}') + \delta(\mathbf{r}-\mathbf{r}')\right)d\mathbf{r}''$$

$$= -\beta\rho kT\left(\rho\int c(\mathbf{r},\mathbf{r}'')h(\mathbf{r},\mathbf{r}')d\mathbf{r}'' - h(\mathbf{r},\mathbf{r}') + c(\mathbf{r},\mathbf{r}') - \frac{\delta(\mathbf{r}-\mathbf{r}'')}{\rho}\right)$$

$$= -\rho^2\int c(\mathbf{r},\mathbf{r}'')h(\mathbf{r},\mathbf{r}')d\mathbf{r}'' + \rho h(\mathbf{r},\mathbf{r}') - \rho c(\mathbf{r},\mathbf{r}') + \delta(\mathbf{r}-\mathbf{r}') = \delta(\mathbf{r}-\mathbf{r}')$$

And we have Ornstein-Zernike relation:

$$h(\mathbf{r},\mathbf{r}') = c(\mathbf{r},\mathbf{r}') + \rho\int c(\mathbf{r},\mathbf{r}'')h(\mathbf{r},\mathbf{r}')d\mathbf{r}''$$